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ORIGINAL CONTRIBUTION

A new crystallization process in polypropylene highly filled with calcium carbonate

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Abstract The influence of high amounts of calcium carbonate filler on the crystallization behavior of polypropylene (PP) is investigated by differential scanning calorimetry (DSC) and fast scanning DSC measurements. The non-isothermal crystallization process at industrially relevant cooling rates of about 100 K/s is significantly influenced by the calcium carbonate filler. Isothermal crystallization measurements indicate a new crystallization process in the temperature range between 45 and 80 °C caused by the filler content. To find an explanation for the origin of this process, we have analyzed the interaction between polymer and filler, the crystalline structure, and the crystallization kinetics. From the experimental results, we conclude that the newly observed crystallization process is governed by an additional nucleation process for the growth of α-phase crystals.

Keywords Crystallization · Calcium carbonate filler · Fast scanning calorimetry

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Introduction

The crystallization during cooling and the isothermal crystallization of polypropylene (PP) have been widely investigated in a large temperature range [1–17]. The use of the fast differential scanning calorimetry (FDSC) technique provides a detailed insight into the kinetics of the crystallization process in a wide temperature range and especially at high supercooling and fast cooling rates [1, 2, 9, 18–21]. From the isothermal crystallization measurements, it is well known that PP shows two different crystallization regimes. The high-temperature regime dominates above 60 °C and manifests itself in the formation of the monoclinic α-phase by heterogeneous nucleation [1, 2, 21]. In the low-temperature regime, the so-called mesophase is formed by, as generally accepted, homogeneous nucleation [1, 9, 22–24]. This phase is interpreted as conformationally disordered, with features intermediate those of the crystalline and amorphous states [5, 9]. Nucleating agents accelerate the high-temperature crystallization process and have practically no influence on the mesophase crystallization [25].

The influence of filler on polymer crystallization is widely studied. Fillers have been classified as active and inactive regarding their nucleation performance. Calcium carbonate (CaCO$_3$) is one of the most common fillers of PP [26]. CaCO$_3$ is usually classified as an inactive filler [27]. For untreated CaCO$_3$, a weak nucleating effect is reported [28, 29]. The influence of CaCO$_3$ on the crystallization process of PP depends on particle shape and surface treatment of the particles [28–31]. Surface treatment can accelerate or slow down the crystallization. A reduction of the overall crystallization is reported for treatment with, e.g., oligomer of ethylene oxide or fatty acids [28, 30]. Differently surface-modified CaCO$_3$ particles stimulate the formation of β-crystals [26, 31, 32]. All these investigations of the crystallization behavior of PP

filled with $CaCO_3$ are performed at relatively low supercooling or low cooling rates. To the best of our knowledge, there is a lack of studies of the crystallization behavior of calcium carbonate-filled PP at industrially relevant supercooling.

In this paper, we study the crystallization behavior of PP highly filled with a commercially available calcium carbonate batch at high supercooling. We have found a crystallization regime in the temperature range between 40 and 80 °C, which was not reported before. The crystallization behavior was analyzed by conventional DSC, fast scanning DSC (Flash DSC), and wide angle X-ray scattering (WAXS).

Experimental

Sample

The measurements were performed using a commercial polypropylene (Borealis HF136MO) with a melt flow index of 20 g/10 min (according to ISO 1133 at 230 °C for 2.16 kg). This material was filled with a commercial calcium carbonate master batch Omyalene 102M-OM. This master batch contains 16 mass% polyolefin blend for compatibilization. The polyolefin component contains mainly PP. The calcium carbonate has particles with an average size of 2.0 μm. The mineral component contains 98 % calcium carbonate. The mineral particles are coated with stearic acid. PP was mixed with the master batch in a mass ratio of 4:6 using a single-screw extruder. Consequently, the filled material consists of about 48 % PP, less than 2 % different incompatible polyolefin, and 50 % coated calcium carbonate filler ($CaCO_3$). The samples were provided by the Plastics Training and Testing Center (KATZ) in Aarau, Switzerland.

Conventional DSC

A METTLER TOLEDO DSC 2 with intracooler and sample robot was used. Sample material of about 5 mg was placed in a 40-μl standard aluminum crucible. The samples were cooled at 30 K/min from 220 to −10 °C and subsequently heated with 30 K/min to 220 °C.

Fast DSC

The Fast DSC measurements were performed using a METTLER TOLEDO Flash DSC 1 with the UFS-1 Sensor [18, 33, 34]. Samples of about 50 ng are deposited directly on the sensor area. Nitrogen was used as a flushing gas, and the surrounding temperature was kept at −50 °C. For the cooling experiments, the samples were cooled from the melt at 190 °C. The cooling rates were varied between 1 and 4000 K/s.

For the isothermal measurements, the samples were cooled from the melt with a rate of 4000 K/s to the target temperature. The filled and unfilled samples were prepared on two different sensors. Both sensors were calibrated with indium after the measurements.

In a pre-study, it was investigated whether the maximum temperature was sufficiently high to prevent memory effects, such as described in [35]. For this, the melt temperature was varied between 180 and 220 °C and the isothermal crystallization at different temperatures between 30 and 90 °C in 10 K steps was measured. As it is shown on the example of unfilled PP in Fig. 1, the crystallization process was not significantly influenced by variation of the melt temperature in this temperature range.

Wide angle X-ray scattering

For the wide angle X-ray scattering (WAXS) measurement, the samples of about 60 mg were molten in a furnace at 220 °C. Afterwards, the samples were rapidly placed on a metallic plate and covered by a metal block. The temperature of the plate and the block was controlled at the crystallization temperature. The final sample thickness was about 0.4 mm. The crystallization temperatures are 95, 65, and 30 °C, respectively. The estimated average cooling rate was faster than 300 K/s. This is evaluated by a worst-case estimation of the cooling time of the center of a 0.4-mm-thick polymer film between metal plates to a temperature 5 K above the metal temperature. This time (0.35 s for 150 K temperature difference) was added by 0.15 s transport time from the furnace.

WAXS measurements were performed in transmission mode using a SAXSLAB Ganesha 300 XL SAXS system operated at near-vacuum conditions with a source-ray photon wavelength of 1.54 Å. Patterns were acquired with an acquisition time of 100 s by means of a Pilatus detector with 487× 619 pixels of 172×172 μm, placed at approximately 100 mm
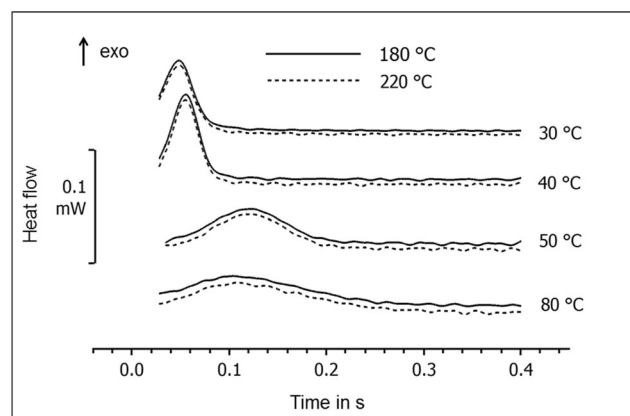

Fig. 1 Isothermal crystallization curves of unfilled PP measured at selected crystallization temperatures. Before crystallization, the sample was heated to 180 °C (*solid lines*) or 220 °C (*dashed lines*)

from the sample surface. All scattering data were background subtracted and integrated using the software package FIT2D (ESRF, France).

Determination of different crystallization processes

Non-isothermal crystallization

From a technical point of view, the crystallization during cooling is most interesting because it simulates the solidification during processing. The conventional DSC cooling measurements of the samples of investigation at a cooling rate of 30 K/min show no significant differences in the crystallization behavior between the filled and unfilled materials (Fig. 2). Flash DSC measurements at faster cooling rates (higher than 50 K/s), however, indicate clear differences between unfilled and filled materials.

In the unfilled material, the high-temperature peak at about 80 °C is related to the α-phase crystallization [1, 2, 21]. The low-temperature peak at 30 °C occurs due to formation of the mesophase [1, 9]. The crystallization in the filled material occurs at lower temperatures than in the unfilled material. In the example of investigation, the $CaCO_3$ filler slightly constrains the overall crystallization at higher cooling rates. The low-temperature event of the bimodal crystallization peak occurs at temperatures above the mesophase crystallization in the unfilled material.

Figure 3 shows the crystallization peak temperatures as a function of cooling rate for both the filled and unfilled materials. The behavior of the unfilled material is in agreement with results of frequently measured isotactic polypropylene at fast cooling rates [15–18, 20]. The high-temperature peak
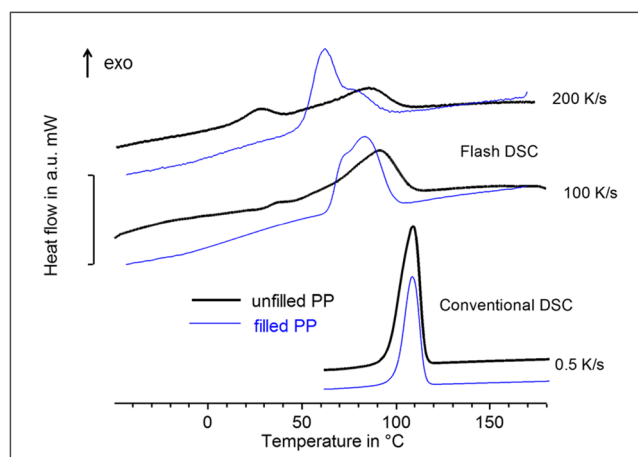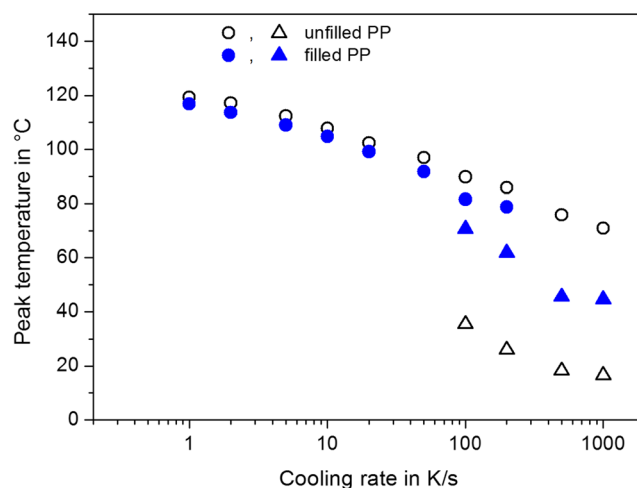

Fig. 3 The peak temperatures of the Flash DSC curves as a function of the cooling rate

shifts continuously to lower temperatures with the increasing cooling rate. At cooling faster than 50 K/s, the second peaks start to appear due to the formation of mesophase content. At cooling faster than 1000 K/s, the peaks disappear because the material stays amorphous.

The filled material shows at the relatively low cooling rates (below 50 K/s) one single crystallization peak. The peak occurs at slightly lower temperatures compared to the unfilled material. Such a behavior is known from conventional DSC measurements of filled PP with surface-modified $CaCO_3$ particles [28, 30]. At rates faster than 50 K/s, the filled material shows a low-temperature crystallization process. However, this process occurs in the temperature range between 70 and 45 °C (Fig. 3). The critical cooling rate to prevent crystallization is similar for the filled and unfilled systems.

Isothermal crystallization

To gain a better understanding of this observed crystallization behavior for the filled material during cooling, isothermal measurements were performed. Figure 4 shows Flash DSC curves measured during isothermal crystallization in the temperature range between 40 and 60 °C.

The crystallization peak time, t_p, is a good approximation of crystallization half-time and is used as a measure for the crystallization rate. The figure clearly shows differences in crystallization behavior between the filled and unfilled samples at this temperature. The isothermal crystallization curves are measured in the temperature range between 0 and 130 °C with an increment of 2 K. In Fig. 5, the peak times are plotted as a function of the crystallization temperature.

The unfilled sample shows the expected bimodal crystallization behavior. The low-temperature process below 60 °C is interpreted as the homogeneously nucleated mesophase

Fig. 2 DSC cooling curves from the melt of unfilled (*thick lines*) and filled (*thin lines*) polypropylene measured with conventional DSC at 30 K/min (*lower curves*) and with Flash DSC at 100 and 200 K/s (*upper curves*). The temperatures of the melt are 220 °C for DSC and 190 °C for Flash DSC, respectively
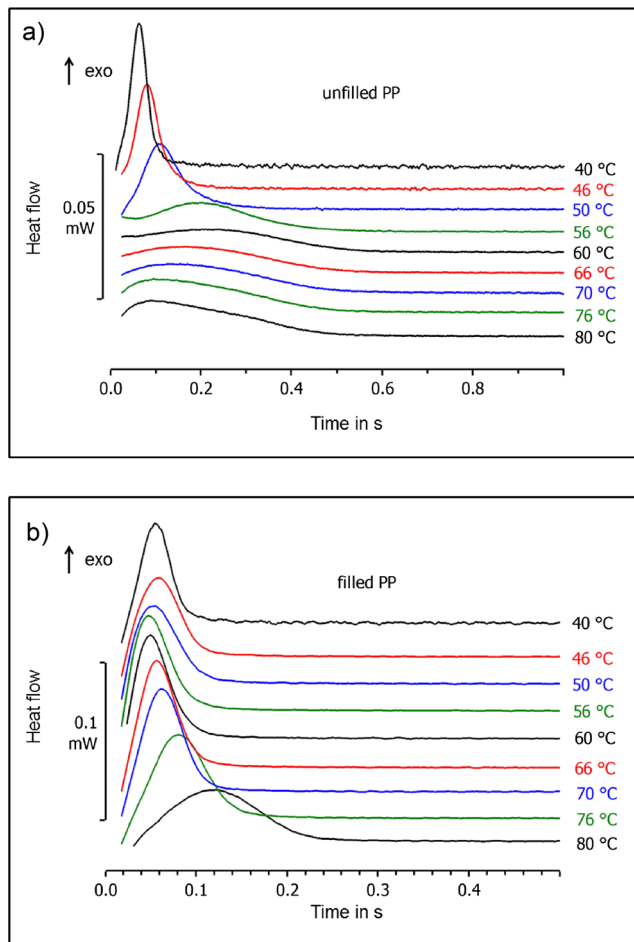
Fig. 4 Isothermal crystallization curves measured at temperatures between 40 and 80 °C of unfilled PP (**a**) and filled PP (**b**)

crystallization. Above 60 °C, heterogeneously nucleated α-phase crystallization occurs [1, 21, 25].
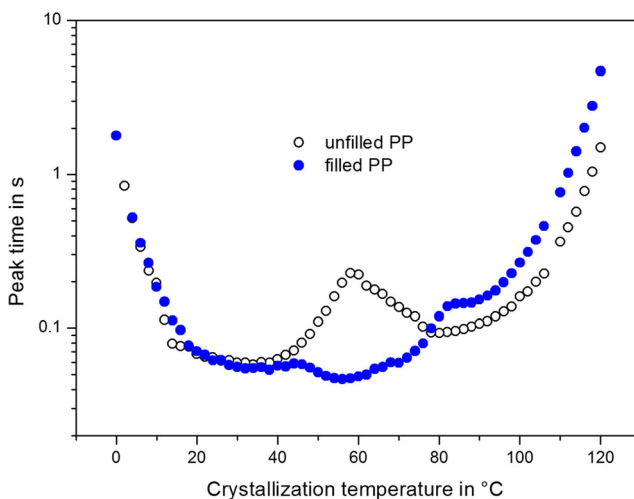

Fig. 5 Crystallization peak time as a function of the isothermal crystallization temperature of unfilled and filled materials

In the range of the mesophase crystallization, the filled and unfilled materials show no significant differences in the peak time. For the high-temperature process, the crystallization rate of the filled material is slightly reduced. Between 45 and 80 °C, however, the filled material shows an additional crystallization process. Between 50 and 65 °C, this process is even faster than mesophase formation. As a consequence, the filled material cannot show the crystallization of the mesophase during cooling, presented in Fig. 3. To our knowledge, this newly observed process between 45 and 80 °C has not been reported before. In the next section, we introduce a first interpretation of the origin of this process.

Discussion

According to the classical crystallization theory of polymers [36, 37], we can characterize the crystallization half-time, $t_{1/2}$, by a diffusion barrier, E_a (apparent activation energy of molecular transport to the growth face of the crystals), and the nucleation barrier, ΔG (the work required for formation of nuclei).

$$t_{1/2} \propto \exp\left(\frac{E_a}{RT} + \frac{\Delta G}{RT}\right) \qquad (1)$$

where R is the gas constant and T is the temperature.

The diffusion barrier E_a is described by the temperature dependence of the relaxation time in the supercooled melt [37] and decreases with increasing temperature.

The nucleation barrier ΔG mainly depends on the type of the formed phase, the type of nucleation, and the surface tension between the crystalline and the amorphous phases. ΔG increases with temperature. At low temperatures, the crystallization process is mainly controlled by the diffusion barrier. The nucleation barrier controls the crystallization process at high temperatures.

With these considerations in mind, the new crystallization regime measured around 60 °C of PP at the presence of the $CaCO_3$ filler can be caused by the following:

- Changes of the diffusion barrier
- Formation of a different phase
- Difference in nucleation

Influence of the $CaCO_3$ particles on the diffusion barrier in the amorphous PP phase

The diffusion barrier is related to the activation energy of the glass transition. A first indication is the comparison of the glass transition temperature, T_g, of the amorphous samples. The glass transition temperatures of the filled and unfilled

materials are measured after cooling with a rate of β_c from the melt and subsequent heating with β_h with $\beta_c = -\beta_h$. Rates between 1000 and 4000 K/s are used. The T_g was determined as the fictive temperature of the glassy state [38]. The glass transition temperatures are plotted in Fig. 6. The differences between T_g measured in heating and cooling are caused by thermal lag [39–41]; the corrected T_g is the average between cooling and heating curves. Figure 6 shows that the corrected glass transition temperatures of the filled and unfilled materials are identical in the order of the experimental uncertainty of about 1 K. This result indicates that the diffusion barrier of crystallization is not significantly influenced by the filler.

From the evaluation of the glass transition, we conclude that the filler does not generate a significant immobilized polymer fraction and does not cause changes in the mobility of the amorphous phase. The diffusion barrier is therefore not the driving factor for the appearance of the additionally observed crystallization process.

Analysis of the involved PP phases

Next, we discuss the possibility that the additional crystallization process is caused by the formation of a different phase in the filled material. The influence of $CaCO_3$ filler on the crystallization of PP at low supercooling has been widely investigated. The filler is frequently discussed as a weak nucleating agent for PP [28, 29]. Some reports discuss the formation of β-phase crystals due to $CaCO_3$ filler [26, 31, 32]. The β-phase formation is related to the surface modification of the filler particles. In β-nucleated PP, the β-phase crystallization was measured at temperatures above 85 °C. At lower temperatures, only α-phase crystallization was observed [2, 25]. To determine the phase which is involved in the additional

crystallization process here, we have characterized the crystal structure by WAXS. The patterns for the unfilled and the filled samples are shown in Fig. 7. In addition to the characteristic alpha crystal diffraction pattern, the first two $CaCO_3$ reflections are detected for the filled system at angles of $2\theta \approx 23.1$ and 29.7, pertaining to the (110) and (211) crystallographic planes, respectively [42]. Only the unfilled material shows the formation of mesophase at 30 °C. All other curves evidence the formation of α-phase crystals. When comparing samples quenched towards 95 and 65 °C, a slight amount of peak broadening is noticed as result of the increased amount of superposed scattering of imperfect crystals, formed at high cooling rates. The formation of other phases next to alpha and mesophase is not detected. The filled sample does not show the mesophase because of the insufficient cooling rate

Fig. 7 WAXS patterns of the unfilled (**a**) and filled (**b**) samples crystallized at 30, 65, and 95 °C. The reflection peaks due to the filler are indicated by *arrows*
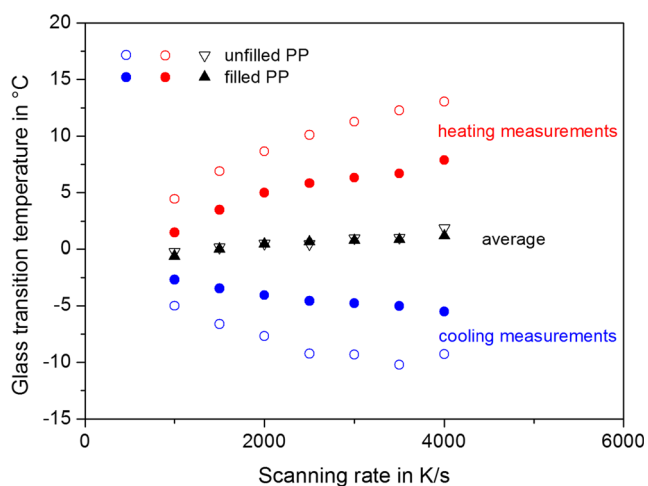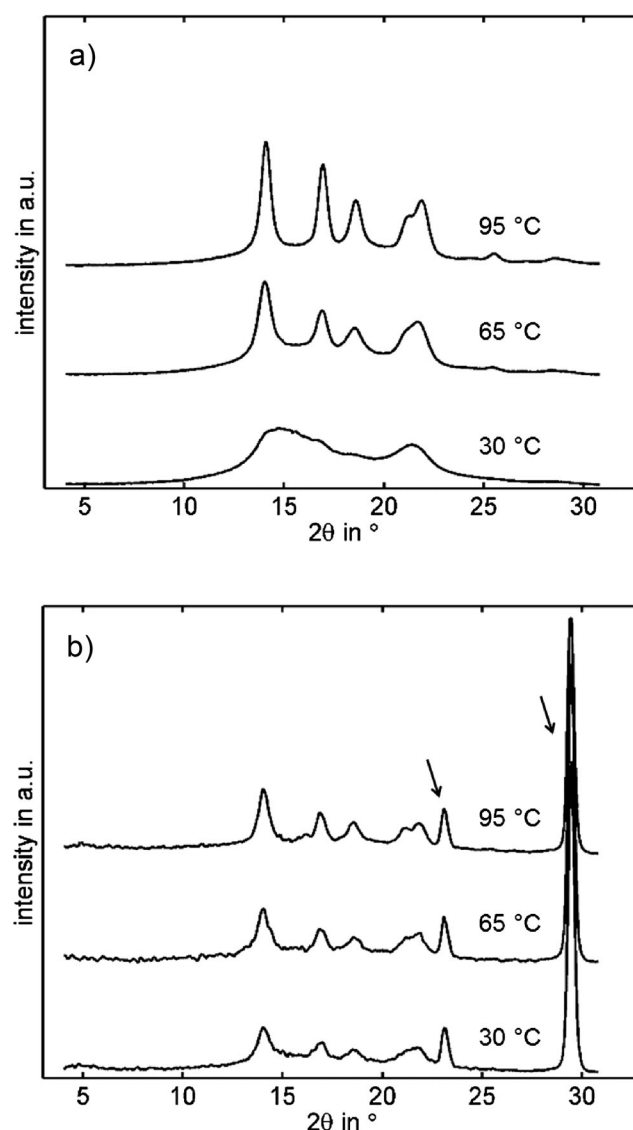
Fig. 6 Glass transition temperature of amorphous filled and unfilled PP, measured at cooling and subsequent heating. The *filled symbols* are for the $CaCO_3$-filled PP, and the *unfilled symbols* are for the unfilled PP

at sample preparation. From Fig. 3, we can estimate that this sample crystallized during cooling at about 50 °C. Consequently, the sample was already crystalline in archiving the nominal crystallization temperature of 30 °C.

As a result of the WAXS measurements, we conclude that in the new crystallization process of the filled material, the α-phase is formed. To prepare mesophase in this sample, a cooling rate faster than 1000 K/s is necessary. For the complete samples with this thickness, such cooling rates are practically impossible.

Different nucleation mechanisms

The new detected crystallization process in the filled material around 60 °C is not caused by a significant change of the diffusion barrier or the formation of a different phase. Therefore, we have to discuss the nucleation process.

Dedicated crystallization events of PP in the interesting temperature range between 45 and 80 °C were reported by Duran et al. [43] and Ibarretxe et al. [44]. In both reports, the material was crystallized in confinements and the considered crystallization process was measured in conventional DSC during cooling at 10 and 5 K/min, respectively.

Duran et al. [43] has studied the confined crystallization of PP in nanoporous alumina with various pore diameters. For large pore diameters, the normal heterogeneously nucleated α-crystallization peak at about 110 °C was measured. At pores of 380 and 180 nm, an additional weak crystallization process at about 73 °C was measured. This crystallization process was interpreted as a homogenously nucleated process because the pore diameter was estimated to be close to the volume of a nucleus. In our cooling measurements, the low-temperature process in the filled material appears at 70.7 °C at a cooling rate of 100 K/s (Fig. 3). This fits well to the process observed in the nanoporous material.

Jin et al. [45] has studied the effect of sorbitol as a nucleation agent in coextruded multi-layer systems of PP and polystyrene (PS). After melting, PP particles in the PS matrix are formed. The particle size was between 0.02 and 0.5 μm. The distribution is centered at about 0.2 μm. In this system, three crystallization effects were measured in the conventional DSC at a cooling rate of 10 K/min. The low-temperature process at 40 °C was characterized as homogeneously nucleated mesophase. The process at 60 °C was interpreted as a formation of "highly defective" α-phase which is "molecularly assisted" homogeneously nucleated [45]. Following the idea in ref. [46, 47], we can interpret a molecularly assisted nucleation as a non-random nucleation (NRN) process. NRN means that subcritical impurities or internal interfaces increase the possibility of nuclei formation compared to the real sporadic nucleation process. The NRN in the small PP particles was supported by the interaction between small amounts of nucleating agent and polypropylene molecules. The nucleation

agent molecules served to stabilize the helical conformation of the PP chain [45]. At higher temperatures, the heterogeneously nucleated α-phase crystallization was observed.

Ibarretxe et al. [44] studied the crystallization of water-dispersed maleic anhydride-grafted polypropylene at droplets with a number average of the diameters between 0.06 and 4.5 μm. Especially the samples with a number average diameter of the droplets of around 2 μm show a crystallization event in between 50 and 60 °C. This crystallization effect is discussed as a consequence of the increase of heterogeneous nuclei in the respective temperature range.

In analogy to these studies, we see two different possible mechanisms for the additional crystallization process in the $CaCO_3$-filled material:

- Homogeneously nucleated formation of α-phase crystals
- NRN nucleation supported by internal interfaces
- The activation of additional heterogeneous nuclei

The small content of incompatible polyolefin of less than 2 % should not significantly influence the crystallization process [48, 49].

Conclusions

The unfilled PP shows two different crystallization processes. During the first and high-temperature process, the α-phase is formed. In the low-temperature range (higher supercooling), mesophase structures are formed.

In the presence of a relatively high content of $CaCO_3$-based filler, an additional crystallization process is measured between the mesophase formation and the heterogeneous nucleated α-phase crystallization. Our measurements exclude that this effect is due to an influence in the molecular mobility in the amorphous phase or the formation of a different crystalline phase. A possible explanation is therefore the activation of additional nuclei. It is not clear whether the nuclei already exist or are formed. In the latter case, non-random nucleation may occur which is supported by the interaction between polymer chain and internal interfaces. Because of the fact that such an intermediate crystallization process was not measured before, neither in nucleated PP nor in PP filled with active filler like carbon nanotubes, we tend to the interpretation that the $CaCO_3$ filler supports non-random nucleation.

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